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# The Catalytic Activity and Selectivity of Acidic Metal Salt Catalysts for *n*-Butene Isomerization

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Double-bond isomerization of *n*-butenes over several supported acidic metal salts such as metal sulfates, perchlorates and phosphates including free acids has been investigated at 60°C with the butene pressure of 14 cmHg. The activity and the selectivity of *cis-trans* isomerization over double-bond migration increased monotonously, as the acid strength of catalysts increased. Acid strength, activity and selectivity of metal salt catalysts increased with the electronegativity of metal ion where free acids were the most strongly acidic and active catalysts ($H^+ > Al^{3+} > Ni^{2+} > Mg^{2+} > Na^+$), and for a given metal ion they increased with the acid strength of the conjugated acid ($ClO_4^- > SO_4^{2-} > PO_4^{3-} > CH_3COO^-$). The activity and selectivity were explained on the basis of a *sec*-butyl carbonium ion mechanism which appears more concerted over weak acids. The active sites for the reaction were suggested to be protonic acid sites closely connected to acid radical.

The simplest and most elementary steps involved in acid catalyzed reactions may be a proton addition to a substrate and its elimination from the protonated complex. It has been established fairly well that the double-bond isomerization of *n*-butenes over most acidic solid catalysts proceeds *via* proton addition to butene followed by its release.[1-3] The *cis-trans* isomerization and the double-bond migration of olefins are referred to as double-bond isomerization, where the hydrocarbon skeleton remains unchanged. Ac-

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[1] A.Ozaki and K.Kimura, *J. Catal.*, **3**, 395(1964).

[2] J. W. Hightower and W. K. Hall, *J. Amer. Chem. Soc.*, **89**, 778 (1967).

[3] Y. Kaneda, Y. Sakurai, S. Kondo, E. Hirota, T. Onishi, Y. Morino, and K. Tamaru, The IVth Intern. Congress on Catalysis, Symposium: Mechanism and Kinetics of Complex Catalytic Reactions, Preprint 12, Moscow, 1968.

cording to the presumed mechanism, a proton transfers to butene from the surface of catalyst forming *sec*-butyl carbonium ion, and then a proton goes back to the surface from the ion leaving isomerized or unisomerized butene. The stereoselectivity in the isomerization of 1-butene to 2-butenes over acidic, basic and metal catalysts have been a subject of many investigations,[4,5] but we have found that the selectivity of *cis-trans* isomerization over double-bond migration of 2-butenes was markedly dependent on the acid strength of catalyst.[6] As the acid strength of metal sulfate increased from $MgSO_4$ to $Al_2(SO_4)_3$ and $H_2SO_4$–$SiO_2$, the rate of isomerization and the selectivity of *cis-trans* isomerization gradually increased by a factor of 10—$10^2$. Furthermore, it was demonstrated that the selectivity of each metal sulfate remained almost constant upon changing the preheating temperature, indicating that the nature of metal ion is the predominant factor determining the acid strength of proton on the surface. It was, therefore, possible to estimate the acid strength of the surface of metal sulfate from the electronegativity of metal ion.[7] The estimated acid strength which was qualitatively confirmed using Hammett's indicators showed linear correlations with the catalytic activity and the selectivity of *cis-trans* isomerization.

All these facts prompted us to study further this system in order to find general relationships which connect each other; the nature of the constituent elements of catalyst, the chemical properties of the catalyst surface, the reaction mechanism and the catalytic activity and selectivity. For this purpose, an investigation using a series of catalysts whose chemical nature varies gradually seems useful.

The purposes of the present paper are i) a more precise investigation of the nature of acid sites developing on the surface of the silica-supported metal sulfates and of the relationship between the selectivity and the kinetics of butene isomerization and ii) the extension of the general rules found for metal sulfates to other metal salts.

## Experimental

*Catalyst Preparation.* Silica-supported metal salts were prepared according to the method described before.[6] Silica gel obtained by the hydrolysis of tetraethoxysilane (*ca* 500 $m^2/g$) was used as support in most cases. Metal sulfates supported on $SiO_2$ are abbreviated hereafter as Al–S for $Al_2SO_4$–$SiO_2$ and Mg–S for $MgSO_4$–$SiO_2$, *etc.* Unless stated otherwise, the amount of supported metal salts was about 5 wt%.

*Butenes, Reaction procedure, Analysis and Acid strength measurement.* They were the same as before,[6] except that the circulation systems with the volumes of 124 and 300 m*l* were used in the present work. The catalysts were evacuated for 1 hr at 100°C in reactors preceding the reaction, unless stated otherwise.

## Results

*Butene isomerization over Al–S and Mg–S.* Figure 1 shows the progress of the reaction of *cis*-2-butene over Mg–S (typical weak acid) and Al–S (typical strong acid) plotted according to the first-order equation

$$\ln (x_e - x) = -\mathbf{k}t + \ln x_e$$

where $x$ and $x_e$ are the conversion at time $t$ and at equilibrium, respectively. This equation does not hold in rigorous sense, because the averaged rate constant of back reaction from 1-butene and *trans*-2-butene depends on the composition of the products which may vary during the course of reaction (see

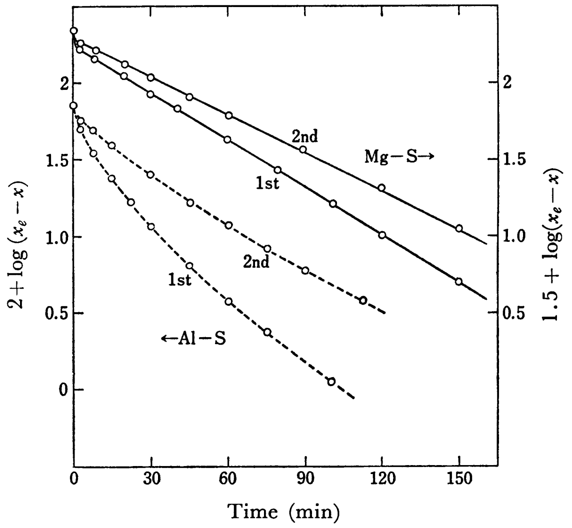

Fig. 1 First-order rate plots for isomerization of *cis*-2-butene over Al-S and Mg-S at 80°C.
Al-S (----, first and second runs), 39 mg
Mg-S (——, first and second runs), 217 mg
Initial pressure: 13.8 cmHg, Circulation system: 124 m*l*

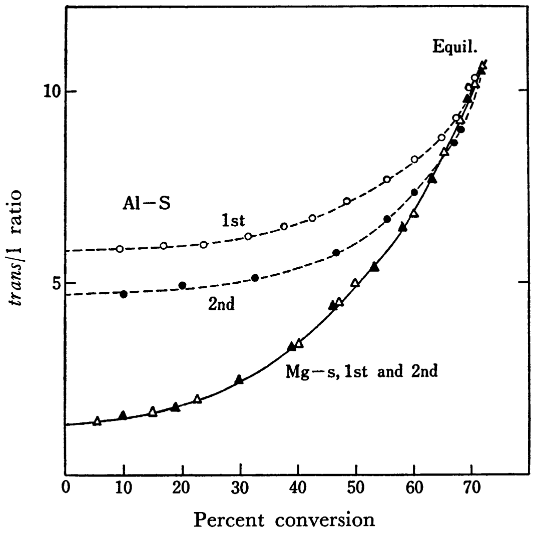

Fig. 2. Composition *vs.* conversion plots for Al-S and Mg-S at 80°C.

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[4] W. O. Hagg and H. Pines, *J. Amer. Chem. Soc.*, **82**, 2488 (1960).

[5] N. F. Foster and R. J. Cvetanovic, *ibid.*, **82**, 4272 (1960).

[6] M. Misono, Y. Saito, and Y. Yoneda, *J. Catal.*, **9**, 135 (1967); **10**, 88 (1968).

[7] M. Misono, E. Ochiai, Y. Saito, and Y. Yoneda, *J. Inorg. Nucl. Chem.*, **29**, 2685 (1967).

Fig. 2). However, this effect is usually small, so that a linear plot is obtained up to a considerably high conversion, if the reaction is of first order for back and forward directions.[2)]

It is seen in Fig. 1 that over Mg–S the reaction follows this equation, except an initial small but rapid deactivation. This plot is very similar to the one obtained by Hightower and Hall over deactivated silica-alumina.[2,8)] Repeated runs resulted in little change in the reaction rate over Mg–S. Over Al–S, on the other hand, a rapid and large deactivation occurred at first and it decreased gradually showing a slow time-dependent poisoning, until a nearly constant rate constant was reached after a long period of reaction. The rate at the apparently stationary stage was about half to one-third the initial one.

These trends in deactivation and their contrast between a weak acid and a strong acid catalyst have been observed in the oligomerization of propylene over differently Na-exchanged silica-alumina and Al–S at the temperature range of 100—300°C.[9)]

Figure 2 shows the changes in the product composition (given by the *trans*-2-butene/1-butene ratio, *trans*/1) during the course of reaction. The *trans*/1 ratio extrapolated to zero conversion, which was nearly equal to the *cis*/1 ratio obtained from *trans*-2-butene for each catalyst, was high for strong acid catalyst and low for weak acid catalyst, as reported before.[6)] The large *trans*/1 ratio for Al–S decreased by the repeated runs as the result of deactivation, while the repeated runs over Mg–S fell on the same line. The end point in Fig. 2 gives the equilibrium ratio of 1:*trans* : *cis*=6 : 66 : 28 (at 80°C). The apparent energies of activation were about 7 kcal/mol for Al–S and about 11 kcal/mol for Mg–S.

Polymerization or coke formation always accompanies the acid catalyzed reaction of olefins.[1,2)] Hightower and Hall[2,8)] and Brouwer[10)] used silica-alumina deactivated by coke formation to obtain reproducible data on the kinetics of butene isomerization. In order to examine the effect of polymerization of butenes (besides the deactivation, there is a possibility of the preferential coke formation of 1-butene which may cause a high *trans*/1 ratio as pointed out by Hightower and Hall[8)]), the rates of polymerization of butenes over Al–S and Mg–S were measured by the pressure decrease. Results are summarized as follows: i) pressure decreased more rapidly over Al–S than over Mg–S, reflecting the difference in the extent of deactivation, ii) there was little difference for each catalyst in the rates of pressure decrease among three butene isomers, and iii) the rate of polymerization was less than 10% of the rate of isomerization.

The results of *cis*-2-butene isomerization over silica-supported aluminum sulfate with various aluminum sulfate contents are shown in Fig. 3. The activity increased almost linearly with the aluminum sulfate content up to∼3 wt% and then showed saturation at higher content of aluminum sulfate. The selectivity (*trans*/1 ratio), on the other hand, remained almost constant over the whole range of the aluminum sulfate content studied. The acid strength of these catalysts also seems to be constant, as seen from the observed colors of the Hammett indicators over these catalysts

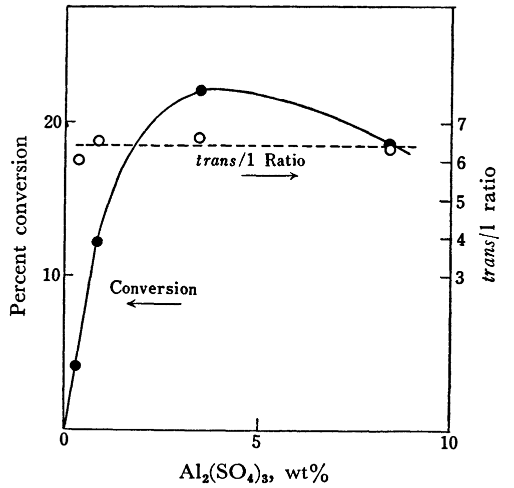

Fig. 3. Effect of amount of supported aluminum sulfate upon catalytic activity and selectivity of *cis*-2-butene isomerization over Al-S at 60°C.

TABLE 1. THE COLOR CHANGES OF HAMMETT'S INDICATORS[a)]

| Catalyst | p$K_a$ of indicator |  |  | *trans*/1 ratio |
|---|---|---|---|---|
|  | +1.5[b)] | −5.6[c)] | −8.2[d)] |  |
| $HClO_4$-$SiO_2$ | + | + | + | 16—20 |
| $Mg(ClO_4)_2$-$SiO_2$ | + | + | + | 7.0 |
| Mg-S | + | − | − | 1.2 |
| Al-S (0.3 wt%) | + | + | + | 6.0 |
| Al-S (3.5 wt%) | + | + | + | 6.6 |
| Al-S-W-2[e)] | + | + | + | 5.0 |
| Al-S-W-3[e)] | + | − | − | 2.4 |
| $SiO_2$[f)] | − | − | − | — |

a) Acidic colors are indicated by+and basic colors by —.
b) benzeneazodiphenylamine
c) benzalacetophenone
d) anthraquinone
e) see Table 2
f) prepared by hydrolysis of tetraethoxysilane.

TABLE 2. EFFECT OF EXTRACTION OF ALUMINUM SULFATE FROM Al-S

| Catalyst | Method of extraction | Relative activity | *trans*/1 ratio |
|---|---|---|---|
| Al-S | original | 1.0 | 6.5 |
| Al-S-W-2 | extracted by water for 10 min | 0.35 | 5.0 |
| Al-S-W-3 | extracted by water several times until the solution became neutral | 0.1 | 2.4 |
| Al-S-W-5 | W-3 was left still water overnight | 0.05 | 1.5 |

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8) J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, **71**, 1014 (1967).
9) M. Misono and Y. Yoneda, This Bulletin, **40**, 42 (1967).
10) D. M. Brouwer, *J. Catal.*, **1**, 22 (1962).

as given in Table 1. These facts again support that the selectivity is determined by the acid strength, while the activity by both the acid strength and acid content. Table 2 shows the changes in the activity and the selectivity upon the extraction of aluminum sulfate by water from Al–S. Both of them decreased rapidly upon the repeated washing. This result is in contrast to the fact given in Fig. 3 that the selectivity remained nearly constant upon the variation of the amount of supported aluminum sulfate.

*Isomerization of* cis-2-*Butene over Silica-supported Metal Salts Other than Metal Sulfate.* The rates of *cis*-2-butene isomerization and the *trans*/1 ratios over silica-supported metal salt catalysts are summarized in Table 3. The rates are given by the conversion at 10 min over 100 mg of catalyst to show the relative activity. Following trends may be remarked in this table: i) For perchlorate salts, the *trans*/1 ratio and the activity increased with the electronegativity of metal ion and the free acid gave the highest values, as observed for metal sulfate catalysts[6] ($H^+ > Ni^{2+} > Mg^{2+} > Na^+$).

TABLE 3. ISOMERIZATION OF *cis*-2-BUTENE OVER VARIOUS SILICA-GEL SUPPORTED METAL SALTS AT 60°C

| Catalyst | Activity[a] | *trans*/1 ratio |
|---|---|---|
| Metal sulfate | | |
| $Al^{3+}$ | 40 | 6.5—7.0 |
| $Ni^{2+}$ | 10 | 2.3 |
| $Mg^{2+}$ | 2 | 1.2 |
| $Na^+$ | no reaction | — |
| Metal perchlorate | | |
| $Ni^{2+}$ (100)[b] | 20 | 11 |
| $Ni^{2+}$ (200)[b] | 4 | 9 |
| $Ni^{2+}$ (300)[b] | 0.4 | 8 |
| $Mg^{2+}$ | 5 | 7 |
| $Na^+$ | very low | 2 |
| Free acid | | |
| $HClO_4$ (60)[b] | 30 | 16—20 |
| $H_2SO_4$ | 40 | 10 |
| $H_3PO_4$ (120)[b] | very low | 2.5 |
| $H_3PO_4$ (200)[b] | 0.1 | 3 |
| Metal chloride | | |
| $Ni^{2+}$ | very low | 1.2 |
| $Mg^{2+}$ | no reaction | — |
| Metal acetate | | |
| $Mg^{2+}$ | no reaction | — |
| Others | | |
| Ion exchange resin (Dowex 50W) | — | 8—10[c] |
| *p*-toluene sulfonic acid | — | 8—20[d] |

a) % conversion after 10 min over 100 mg of catalyst.
b) Evacution temperature. Others were evacuated at 100°C.
c) Ref. 4.
d) Ref. 6.

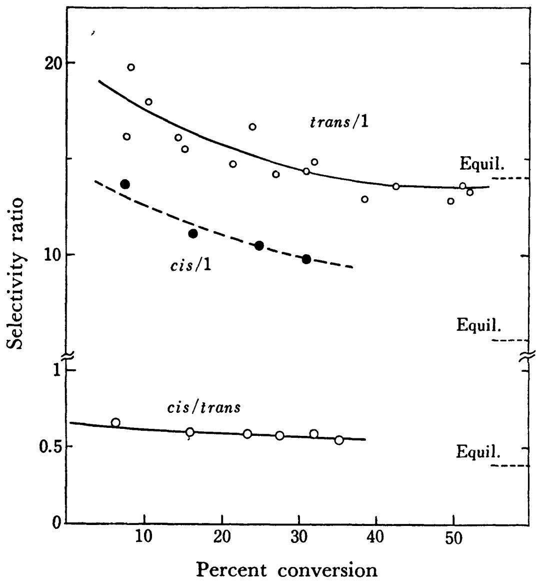

Fig. 4. Composition *vs.* conversion plots of isomerization of butenes over silica-supported perchloric acid at 60°C. *trans*/1 ratio decreased once below the equilibrium ratio due to rapid deactivation and then recovered to the equilibrium one.

ii) For the salts of a given metal ion, they were in the order of the acid strength of the conjugated acid ($ClO_4^- > SO_4^{2-} > PO_4^{3-} > CH_3COO^-$).

iii) As for free acids, both activity and *trans*/1 ratio decreased as $HClO_4 > H_2SO_4 > H_3PO_4$. Over $HClO_4$–$SiO_2$, *cis*/1 from *trans*-2-butene was ~14 and *cis*/*trans* ratio from 1-butene ~0.7. It is clearly seen that not only the *cis*/1 ratio but also the *trans*/1 ratio exceeded the equilibrium ratio (Fig. 4), although the data rather scattered.[11]

iv) Metal chloride and acetate catalysts gave very low or no activity for this reaction.

The acid strength measured by indicators (Table 1) well explains the activity and *trans*/1 ratios as was done in the previous work for metal sulfates.[6] For example, the *trans*/1 ratio increased from 1.2 for Mg–S to 7.0 for $Mg(ClO_4)_2$–$SiO_2$, where the acid strength of Mg–S was comparable with that of benzeneazodiphenylamine ($pK_A = 1.5$) and $Mg(ClO_4)_2$–$SiO_2$ was more strongly acidic than anthraquinone ($pK_A = -8.2$).

Finally, the effect of different silica gels as support may be mentioned. Little effect on the activity and the selectivity was observed for the active catalysts such as Al–S. However, there was a little increase in activity in the case of the catalysts having very low activity such as Mg–S and $NiCl_2$–$SiO_2$ when more acidic silica gel was used as support, although the activities of the supports alone were always much lower than $NiCl_2$–$SiO_2$.

## Discussion

Essential parts of the results obtained previously about the double-bond isomerization of butenes over metal sulfate catalysts were as follows.[6]

i) The acid strength of metal sulfate catalyst was primarily determined by the electronegativity of the

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[11] Results of several experiments were plotted for *cis*-2-butene isomerization. The scattering of data was due to the rapid deactivation of catalyst, and there existed systematic trend in scattering which will be fully discussed in the forthcoming paper.

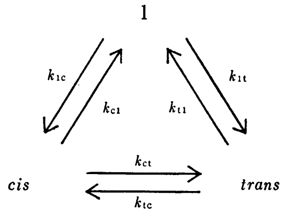
constituent metal ion.

ii) The acid strength controls the selectivity of *cis-trans* isomerization over double-bond migration. The activity is determined by both acid strength and content.

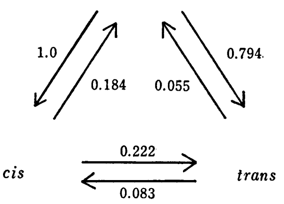
iii) The selectivity change was interpreted by the change in the relative rates of proton addition to butene and proton elimination. These rates are expected to vary with acid strength.

The results obtained in the present work for the supported metal perchlorates, sulfates and phosphate (including free acids) (Tables 1 and 3) demonstrate that the acid strength of metal salt catalysts, at least salts of oxy acids, can be controlled not only by changing the metal ion but also by changing the anion. The *trans*/1 ratios and the acid strength given in those tables follow, in general, the expected order of the "intrinsic" acid strength of metal salts. The "intrinsic" acid strength is referred to as the acid strength related directly to the properties of the constituent atoms or groups of the substance. This might be expressed, for example, by the pH of aqueous solution of the metal salts, if one can neglect the leveling effect. If the general trend between the acid strength and the selectivity is applicable to silica-alumina, the *trans*/1 or *cis*/1 ratio over silica-alumina should be as high as those for Al–S and $H_2SO_4$–$SiO_2$, since its acid strength is as strong as that of Al–S.[9,12] Reported *trans*/1 or *cis*/1 ratio for silica-alumina ranges from 1 to 7.[1,2,5,8,10] However, it may be noted that Hightower and Hall[8] reported that the *trans*/1 ratio over fresh silica-alumina was about 7, which diminished rapidly down to almost unity by the repeated runs and that most of the previous data were obtained over more or less deactivated catalysts.

*Acid Strength and Reaction Mechanism.* The selectivity ratio (*trans*/1 or *cis*/1) increased from Mg–S to Al–S with the increase in the catalytic activity. As the equilibrium favors 2-butene formation, secondary isomerization from 1-butene to 2-butene could have effected the high selectivity ratio for active catalysts. However, this possibility can be rejected, since the selectivity ratios higher than the equilibrium ones were found; *e.g.*, *cis*/1 ratios were 14, 10, and 6 for $HClO_4$–$SiO_2$, $H_2SO_4$–$SiO_2$ and Al–S, respectively, where the equilibrium ratio is 5.4, and the *trans*/1 over $HClO_4$–$SiO_2$ was 16—20, as compared with the equilibrium ratio of 14.4 (Table 3 and Fig. 4). The preferential polymerization of 1-butene as the reason of high *trans*/1 or *cis*/1 ratio suggested by Hightower and Hall[8] is also denied, because this side reaction was less than 10% of the isomerization and little difference was observed among the rates of pressure decrease of three butene isomers. Therefore, the observed selectivity ratio may safely be considered as the ratio of the rates of two paths from a butene isomer. Further, the relationships found among three selectivity ratios for each catalyst, that is, (*trans*/1) (1/*cis*) (*cis*/*trans*) = 1,[4,6] indicate that the reaction orders of isomerizations were nearly identical for each catalyst, so that the observed ratios may be considered as the ratios of the rate constants; *viz.*, *trans*/1, *etc.* are $k_{ct}/k_{c}$, *etc.* in the following reaction scheme.



The relative rate constants can be calculated utilizing equilibrium and selectivity ratios as an example for Mg–S at 60°C as follows[4,8]

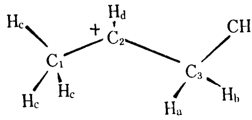


Suppose a simple reaction catalyzed by acid, consisting of a proton addition and elimination,

$$A + H^+ \rightarrow (M) \qquad (1)$$

$$(M) \rightarrow B + H^+ \qquad (2)$$

where A, B, and M are reactant, product and protonated reaction intermediate, respectively. In step (1), a catalyst acts as an acid and in the next step as a base. As the acid strength increases, the rate will increase initially by the acceleration of step (1) and then diminish upon further increase in the acid strength due to the slow rate of step (2), showing a volcano-type activity pattern.[13,14] This concept may be applied in the present case, since it seems generally accepted that double-bond isomerization of butenes catalyzed by solid acids such as silica-alumina and metal sulfate proceeds through proton addition to form a *sec*-butyl carbonium ion (step(1)) and elimination of proton from the complex (step(2)).[1,2,6,8,10], If one accepts this mechanism, one may expect that over a strong acid the proton addition occurs readily and the carbonium ion is stable. This step would be slow and the ion is unstable over a weak acid. Considering a *sec*-butyl carbonium ion, the proton release from C–$H_a$ would tend to result into *cis*-2-butene formation, from C–$H_b$ into *trans*-2-butene and from one of C–$H_c$ into 1-butene.[8] Since two $C_3$–H bonds of methylene may be energetically similar and differs from those of methyl ($C_1$–$H_c$), it is under-



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12) J. Take, T. Tsuruya, T. Sato, and Y. Yoneda, to be published.

13) M. Misono, *Shokubai (Catalyst)*, **9**, 252 (1967).

14) O. A. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John-Wiley and Sons, New York (1963), p. 163.

standable that among various catalysts the *trans*/1 and *cis*/1 ratios were always nearly identical and were different from the *cis*/*trans* ratio which was almost unity.[6)]

The changes in 2-/1-butene ratios (*trans*/1 and *cis*/1) may be explained by the variation in the transition state and the relative rates of proton addition and elimination as follows. According to Hammond[15)] and Leffler and Grunwald,[14)] the transition state of a reaction step more nearly resembles the reactant as the step becomes more exothermic. This postulate calls for, in other words, the transition state of a bond rupture step to involve relatively less bond breakings when the bond is easily broken and relatively more when it is difficult to break. If one applies this postulate to the proton elimination from carbonium ion, the transition state is expected to reflect more the final state, butene, as the ion becomes more stable as over a strong acid. The formation of stable 2-butenes is, therefore, favored over a strong acid. If the carbonium ion is less stable as over a weak acid, the transition state resembles the initial state, the ion, reflecting to a less degree the product, or butene, so that the 2-/1-butene ratio approaches unity. Furthermore, as the acid strength decreases, proton addition would become more difficult and tend to occur almost simultaneously with proton elimination. Then the isomerization reaction will appear more concerted over a weak acid: double-bond migration will increase, relative to *cis-trans* isomerization.

A similar interpretation can be found in the elimination reaction *via* carbonium ion (El mechanism).[16)] As the acid strength of a solvent, a nucleophilic reagent or a catalyst decreases, the reaction mechanism changes from El to E2 like mechanism:

$$\text{(El mechanism)} \quad RX + A \rightarrow R^+ + XA$$

$$R^+ \rightarrow R' + H^+$$

By the El mechanism, *sec*-butyl bromide or tosylate gave the butene mixture in the composition of 1 : *trans* : *cis*=5∼7 : 41∼46 : 47∼54 (high 2-/1-butene ratio), while it was 23 : 18 : 59 by E2 mechanism (low 2-/1-butene ratio).[17)] When a very unstable carbonium ion is formed as in the elimination of amino group from *sec*-butylamine catalyzed by $HNO_2$, the composition of butenes was 22 : 25 : 53.[17)]

*Active Acid Sites for the Double-Bond Isomerization of Butenes.* Since 2-/1-butene ratio reflects the acid strength,[6)] little variation in the *trans*/1 ratio found upon changing the amount of supported aluminum sulfate (Fig. 3) and the preheating temperature,[6)] suggests that a certain and definite interaction between silica gel surface and aluminum sulfate developed the acid sites active for the isomerization. These sites must be protonic (Brönsted type) from the following reasons, although the electronegativity of metal ion which expresses the acid strength of a metal ion as Lewis acid[7)] linearly correlated with the selectivity and the catalytic activity.[6)]

i) Deuteration of isomerized butenes took place during the reaction over deuterated $NiSO_4$–$SiO_2$,[1)] *p*-toluene sulfonic acid[3)] and silica-alumina.[2)]

ii) Supported free acids were the most active catalysts and gave the highest *trans*/1 ratios among the series of metal salts of a given acid (Table 3).

iii) $NiCl_2$–$SiO_2$ and $MgCl_2$–$SiO_2$ were much less active or inactive as compared to Ni–S or Mg–S. One might be allowed to expect some activity for the formers, if the metal ions themselves are active.

iv) The rate of isomerization decreased upon deuteration of the catalysts (catalyst isotope effect).[18)]

This protonic site active for the isomerization is not likely to be a proton in silanol group which may exist and whose acid strength may vary by the metal ion. But it seems to be a proton closely connected to sulfate or perchlorate ion, since 1) the activity and *trans*/1 ratio, as well as the acid strength, strongly depended on the acid strength of anion (Tables 1 and 3), 2) metal chloride catalysts were not active, even though Me–O–Si–OH were reported to exist for these catalysts,[19)] and 3) an ion exchange resin (sulfonic acid type)[6)] and *p*-toluene sulfonic acid[3)] whose acid sites must be $SO_3H$ gave the *trans*/1 ratio and activity as high as $H_2SO_4$–$SiO_2$ and $HClO_4$–$SiO_2$. As the electronegativity represents the power of atom or an ion to attract electron, the role of metal ion may be lowering the electron density of oxygen of –OH, promoting the tendency of the proton to dissociate. The effects of the electronegative group on the acidity was postulated for fluorine treated silanol group.[20)] The rapid decrease in the *trans*/1 ratio and the activity upon washing out of aluminum sulfate (Table 2) indicates that the structure of active acid sites is very soluble in water and is, therefore, different from the one reported by Burne et al.[21)]

*Polymerization on the Surface as the Origin of Deactivation.* The pressure decrease observed during isomerization was rapid initially and then the rate reached nearly constant. This process was fast over strong acids and was slow and small over weak acids. These trends closely resemble those found in the case of propylene oligomerization over silica-aluminas with various acid strengths.[9)] As in propylene oligomerization and butene isomerization over silica-alumina,[2,8)] the polymerization or coke formation from butene is likely to be the primary origin of deactivation in the present case and the acid strength decreased by the deactivation.

The authors are indebted to Professor Y. Saito for helpful discussions. Partial support by the Kawakami Foundation is gratefully acknowledged.

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